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Opportunities and limitations of perovskite - fluorite composite ceramic electrodes

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The most popular materials utilized in R&D of solid oxide electrochemical cells (SOCs) are metal oxides with fluorite (MO_2 , $M = \text{Zr, Ce, Hf, Th, U}$) and perovskite (ABO_3 , $A = \text{large cation, B} = \text{small cation}$) related structures. These compounds are extremely flexible with respect to substitution of host cations and non-stoichiometry. This opens the possibility of doing materials engineering to a large extent, i.e. the possibility of tailoring the basic materials properties. There is, especially for the perovskites, an almost infinite number of possible combinations of metal ions as multi-substitutions on both A and B sites can be performed..

The materials are being used or developed for many applications, e.g. solid oxide fuel cells, electrolyser cells, gas cleaning cells, potentiometric oxygen sensors, dense membranes for separation of oxygen and hydrogen from other gases, catalysts, and many other purposes. The opportunity of creating mixed ionic and electronic conductors (MIECs) is essential in almost all of the mentioned examples. However, there are many strong/strict demands to the materials, e.g. an SOFC requires at least:

- stability in hydrogen and/or oxygen,
- high electronic and ionic conductivity,
- high surface exchange rate of reactant gases (= high electrocatalytic activity),
- matching thermal expansion coefficient,
- single phase material from room temperature to sintering temperature

All these wanted properties cannot be obtained in one material, and thus there is a need for making composites of two or more materials with different properties.

This "jungle" of opportunities and limitations raises a need for optimization tools or rules, which can guide us to the materials or material combinations that are needed. Many attempts of establishing rules based on a fundamental understanding of the perovskite and fluorite crystal chemistry have been made during the latest decades. A critical review of published hypotheses was carried out by the present author and colleagues 6 years ago [1]. This analysis concluded that of the several parameters, which were claimed to be important for the ionic conductivity, only two seemed really essential, namely: a high symmetry, and a low distortion of the crystal lattice. Further, it was pointed out that these two parameters are not independent but actually both these and most other parameters that were claimed important are closely related to the ionic radii of the cations. Also, the literature indicated that the non-distorted lattice would accept a much higher concentration of mobile vacancies than a distorted lattice.

Since then, work on the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) materials as oxygen separation membrane and SOFC cathode, see e.g. [2,3,4,5], has proven that our analysis [1] is insufficient. The Ba^{2+} ion has much too big a radius to leave the perovskite structure stress free but in spite of this the vacancy concentration is higher than in most other doped perovskites. A tentative explanation of this fact

may be that the free enthalpy of formation of oxide vacancies is a balance between the oxygen metal bond strength and the lattice distortion, i.e. the lower the bond strength, the lower the positive value of the vacancy formation enthalpy, which in turn implies a higher vacancy concentration. On the other hand large distortions will tend to trap the vacancies in the stress field associated with the too big cations. This will be further discussed.

Another parameter closely related to the vacancy concentration is the oxygen exchange rate, which actually is very high for fresh BSCF surfaces. However, BSCF also displays one of the significant limitations of perovskites, namely the tendency of the big A-site ions to segregate to the surface and react with air components like CO_2 thus forming inactive and possibly blocking layers on the surface by which the electrode degrades very fast. This is also a lifetime limitation for other kinds of perovskite SOFC cathodes [3,4,5].

The presentation will also briefly cover the limitations in making composite electrodes caused by the reactivity of perovskite with zirconia based electrolyte. This reactivity is closely related to the ionic radii of the cations of the perovskite and the fluorite.

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